

PATENT COOPERATION TREATY

15.12.2004 15.12.2004

CB Z. Ktw.

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

M. 12.04
CB

To:

BASELL POLYOLEFINE GMBH
Intellectual Property Departement
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Basell Intellectual Property

03. Dez. 2004

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year)

02.12.2004

Applicant's or agent's file reference
LU6059/CB

IMPORTANT NOTIFICATION

International application No.
PCT/EP 03/11678

International filing date (day/month/year)
22.10.2003

Priority date (day/month/year)
25.10.2002

Applicant

BASELL POLYOLEFINE GMBH et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international preliminary examining authority:



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D-80298 Munich
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D. Tamik Müller, 15.12.04

CB

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)


REC'D 03 DEC 2004

WIPO PCT

Applicant's or agent's file reference LU6059/CB	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/EP 03/11678	International filing date (day/month/year) 22.10.2003	Priority date (day/month/year) 25.10.2002
International Patent Classification (IPC) or both national classification and IPC C08F4/60		
Applicant BASELL POLYOLEFINE GMBH et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).
- These annexes consist of a total of 13 sheets.

3. This report contains indications relating to the following items:
- I ☒ Basis of the opinion
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☐ Certain documents cited
 - VII ☐ Certain defects in the international application
 - VIII ☐ Certain observations on the international application

Date of submission of the demand 07.05.2004	Date of completion of this report 02.12.2004
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Elliott, A Telephone No. +49 89 2399-8218



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/EP 03/1678**

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17):*

Description, Pages

1-33 as originally filed

Claims, Numbers

1-15 filed with telefax on 26.08.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/EP 03/11678**

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-15
	No: Claims	-
Inventive step (IS)	Yes: Claims	1-15
	No: Claims	-
Industrial applicability (IA)	Yes: Claims	1-15
	No: Claims	-

2. Citations and explanations

see separate sheet

The application relates to racemic metallocenes of formula (I), to methods for their preparation and to their use as a catalyst or as a constituent of a catalyst for the polymerisation of olefinically unsaturated compounds or a reagent or catalyst in stereoselective synthesis.

The following documents are referred to in this report:

- D1: EP-A-1 275 662 (SUMITOMO CHEMICAL CO) 15 January 2003 & WO 02/051878 a (SUMITOMO CHEM CO LTD) 4 July 2002
D2: EP-A-0 997 480 (MARUZEN PETROCHEM CO LTD) 3 May 2000
D3: WARTCHOW, RUDOLF ET AL: 'Synthesis and characterization of rac-[ethylene-1,2-bis(η^5 -4,5,6,7-tetrahydro-1-indenyl)]zirconium bisamides (EBTHI)Zr(NHR)₂' JOURNAL OF ORGANOMETALLIC CHEMISTRY (1998), 566(1-2), 287-291
D4: WO 02/00672 A (BASELL POLYOLEFINE GMBH) 3 January 2002
D5: BOCHMANN, MANFRED ET AL: 'Base-free cationic zirconium benzyl complexes as highly active polymerization catalysts' ORGANOMETALLICS (1993), 12(3), 633-40

V Reasoned statement under Art 35(2) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement

V.i Novelty (Article 33(2) PCT)

With the subject-matter of the claims being restricted to compounds where the metal is selected from titanium, zirconium and hafnium and, more importantly, where Y is Oxygen, novelty can be acknowledged over the prior art (the subject-matter of claims **3-5,7,9 & 16** as originally filed was not considered new with respect to document D3, in particular compound 3a and its use described in D3).

V.ii Inventive Step (Article 33(3) PCT)

The subject-matter of claims **1-16** is to be regarded as being based upon an inventive step on the following grounds:

although documents D1 (here it is assumed that the EP version in English corresponds to the WO version in Japanese) and D2 given generic disclosures of the presently-claimed compounds (cf. D1, the whole document concentrating on the definitions given or X, especially those definitions given in paragraphs [0193] and [0195] and D2, paragraphs [0011] and [0019]) and their use, D1 and D2 fail to disclose how to prepare solely the racemic form of the compounds as compared to a mixture of the racemic and meso forms. The fact that the present inventors have achieved a process to prepare the presently-claimed compounds which are solely in

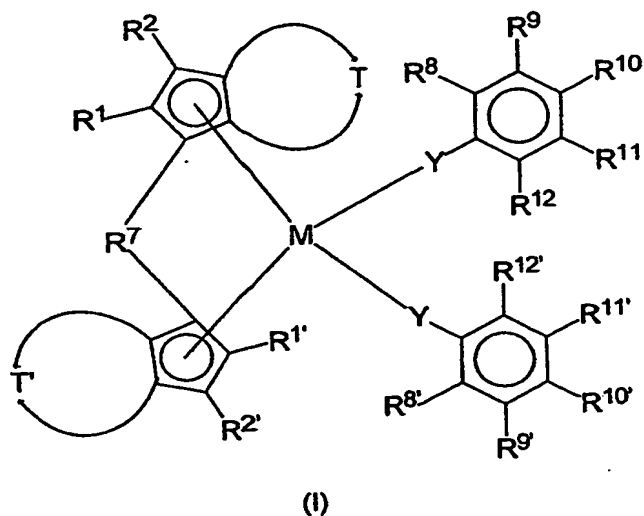
the racemic form is an indication of the inventive merit of the presently-claimed subject-matter. The method in which the racemic metallocenes are prepared in D3 is fundamentally different to that of the present application as a racemic zirconocene dichloride is reacted with an amide - compare that with the present application which takes a diphenoxy metal compound and reacts this with the dicyclopentadienyl compound which by the presently-claimed method produces the racemic metallocene without the need for a racemic metallocene as a starting material.

Other matters:

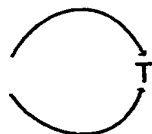
Documents D1-D5 should be briefly discussed in the description (Rule 5.1(a)(ii) PCT).

We claim:

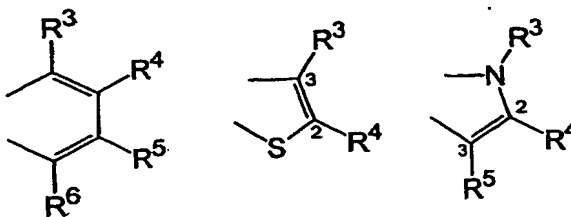
1. A process for preparing racemic metallocene complexes of the formula (I)



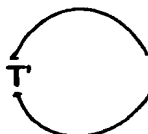
where



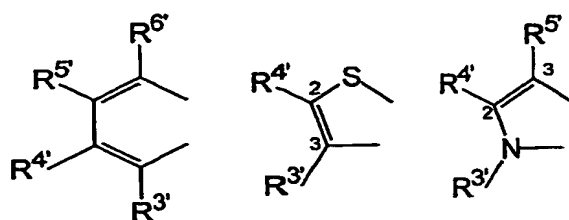
is a divalent group such as:



and



is a divalent group such as



and the substituents and indices have the following meanings:

M is titanium, zirconium or hafnium,

$R^1, R^2, R^3, R^4, R^5, R^6, R^9, R^{10}, R^{11}, R^{1'}, R^2, R^3, R^4, R^5, R^6, R^9, R^{10}, R^{11}$ are identical or different and are each hydrogen, halogen, C_1-C_{20} -alkyl, 3- to 8-membered cycloalkyl which may in turn bear a C_1-C_{10} -alkyl group as substituent, C_6-C_{15} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, arylalkyl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part,

$-OR^{13}, -SR^{13}, -N(R^{13})_2, -P(R^{13})_2$, or $Si(R^{13})_3$, where R^{13} are identical or different and are each C_1-C_{10} -alkyl, C_6-C_{15} -aryl, C_3-C_{10} -cycloalkyl, alkylaryl, where the radicals mentioned may be partially or fully substituted by heteroatoms,

R^8, R^{12}, R^8, R^{12} are identical or different and are each C_1-C_{10} -alkyl,

Y are oxygen -O-

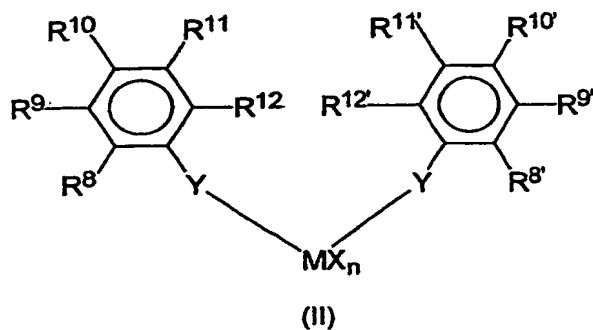
R^7 is a $-[Z(R^{15})(R^{16})]_m-$ group, where

Z can be identical or different and are each silicon, germanium, tin or carbon,

R^{15}, R^{16} are each hydrogen, C_1-C_{10} -alkyl, C_3-C_{10} -cycloalkyl or C_6-C_{15} -aryl,

m is 1, 2, 3 or 4,

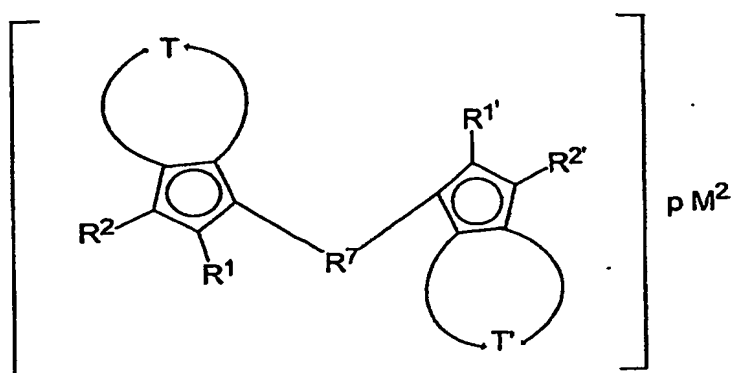
by reacting a transition metal complex of the formula (II)



where

X are identical or different and are each hydrogen, halogen, C₁-C₁₀-alkyl, C₆-C₁₅-aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, -OR¹⁷ or -NR¹⁷₂, where R¹⁷ are identical or different and are each C₁-C₁₀-alkyl, C₆-C₁₅-aryl, C₃-C₁₀-cycloalkyl, alkylaryl, n is an integer from 1 to 4 and corresponds to the valence of M minus 2,

with cyclopentadienyl derivatives of the formula (III)



where

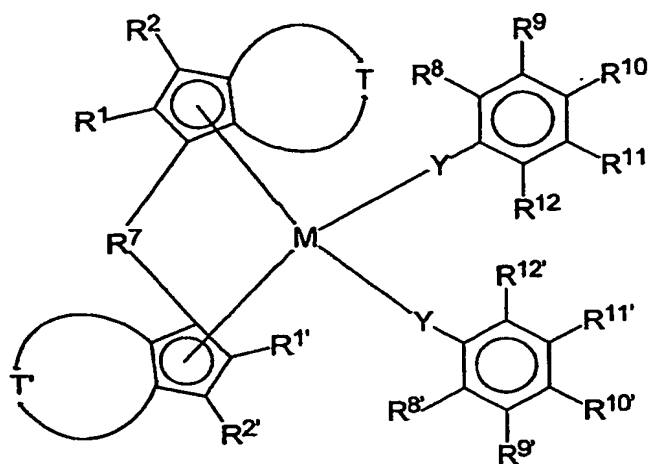
M² is an alkali metal ion or alkaline earth metal ion,

and

p is 1 when M² is an alkaline earth metal ion and is 2 when M² is an alkali metal ion,

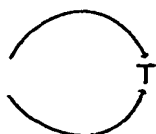
and heating the resulting reaction mixture to a temperature in the range from -78 to +250°C.

2. A process as claimed in claim 1 for preparing racemic metallocene complexes of the formula (I)

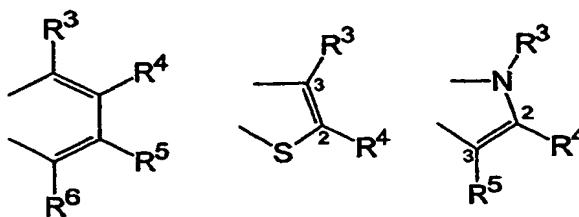


(I)

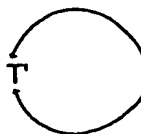
where



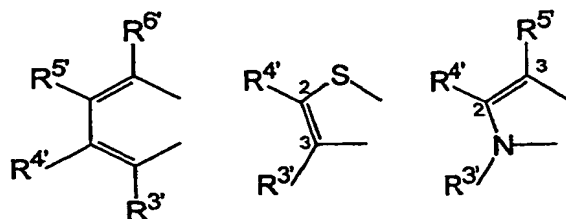
is a divalent group such as



and



is a divalent group such as



and the substituents and indices have the following meanings:

M is titanium, zirconium or hafnium,

$R^1, R^2, R^3, R^4, R^5, R^6, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}$ are identical or different and are each hydrogen, halogen, C_1 - C_{20} -alkyl, 3- to 8-membered cycloalkyl which may in turn bear a C_1 - C_{10} -alkyl group as substituent, C_6 - C_{15} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, arylalkyl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part,

R^{13} $-OR^{13}, -SR^{13}, -N(R^{13})_2, -P(R^{13})_2$ or $Si(R^{13})_3$, where are identical or different and are each C_1 - C_{10} -alkyl, C_6 - C_{15} -aryl, C_3 - C_{10} -cycloalkyl, alkylaryl, where the radicals mentioned may be partially or fully substituted by heteroatoms,

R^8, R^{12}, R^8, R^{12} are identical or different and are each C_1 - C_{10} -alkyl,

Y are oxygen $-O-$

R^7 is a $-[Z(R^{15})(R^{16})]_m-$ group, where

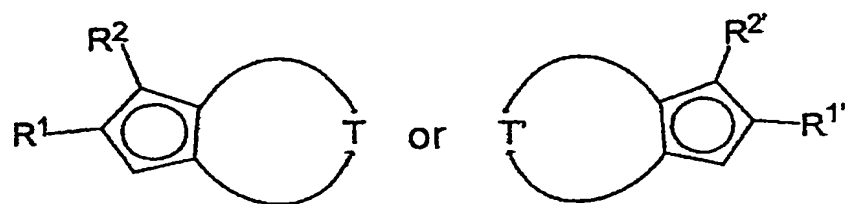
Z can be identical or different and are each silicon, germanium, tin or carbon,

R^{15}, R^{16} are each hydrogen, C_1 - C_{10} -alkyl, C_3 - C_{10} -cycloalkyl or C_6 - C_{15} -aryl,

m is 1, 2, 3 or 4,

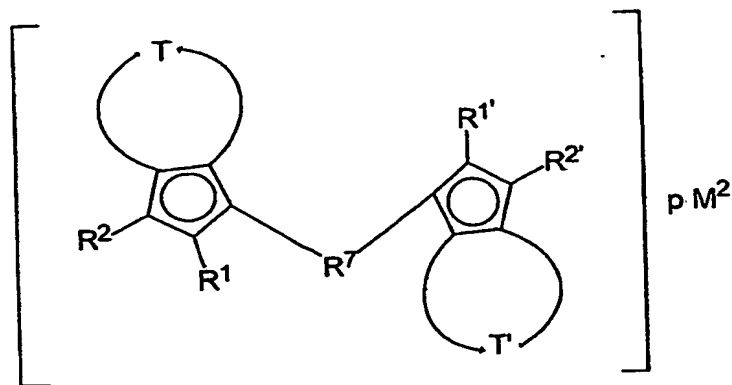
comprising the following steps:

a) deprotonation of a compound of the formula (IV)



(IV)

by means of a suitable deprotonating agent;
 b) reaction of the deprotonated compound (IV) with a compound R^7Hal_2 , where Hal is a halogen substituent such as F, Cl, Br or I, and subsequent repeat deprotonation by means of a suitable deprotonating agent to give the compound of the formula (III)



(III)

where

M^2

is an alkali metal ion or alkaline earth metal ion,

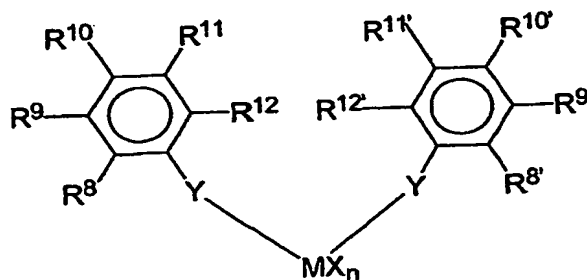
where

p

is 1 when M^2 is an alkaline earth metal ion and is 2 when M^2 is an alkali metal ion, and R^7 is as defined above;

b)

reaction of the compound of the formula (III) with a transition metal complex of the formula (II)



(II)

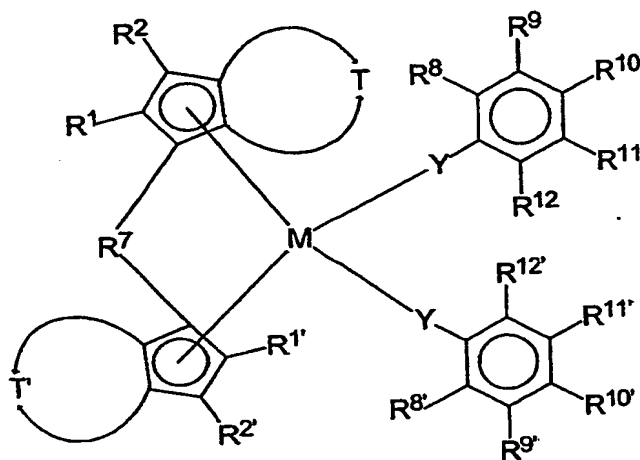
where

X

are identical or different and are each hydrogen, halogen, C_1-C_{10} -alkyl, C_6-C_{15} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, $-OR^{17}$ or $-NR^{17}_2$, where R^{17} are identical

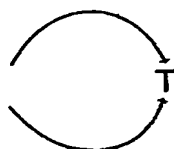
to 20 carbon atoms in the aryl part, $-OR^{17}$ or $-NR^{17}_2$, where R^{17} are identical or different and are each C_1 - C_{10} -alkyl, C_6 - C_{15} -aryl, C_3 - C_{10} -cycloalkyl, alkylaryl, n is an integer from 1 to 4 and corresponds to the valence of M minus 2, and the other substituents are as defined above.

3. A racemic metallocene complex of the formula (I)

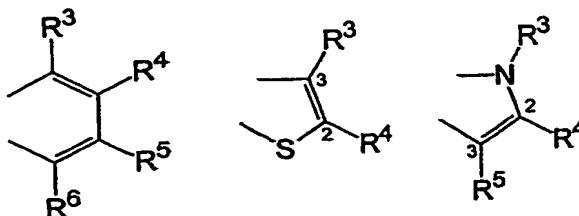


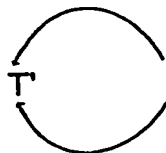
(I)

where

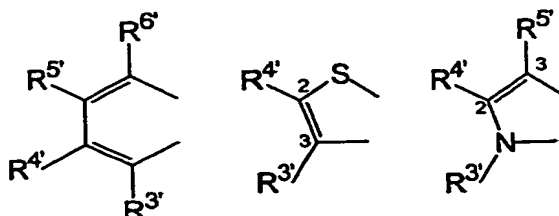


is a divalent group such as





is a divalent group such as



and the substituents and indices have the following meanings:

M is titanium, zirconium or hafnium,

$R^1, R^2, R^3, R^4, R^5, R^6, R^9, R^{10}, R^{11}, R^{1'}, R^2, R^3, R^4, R^5, R^6, R^9, R^{10}, R^{11}$ are identical or different and are each hydrogen, halogen, C_1-C_{20} -alkyl, 3- to 8-membered cycloalkyl which may in turn bear a C_1-C_{10} -alkyl group as substituent, C_6-C_{15} -aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, arylalkyl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, $-OR^{13}$, $-SR^{13}$, $-N(R^{13})_2$, $-P(R^{13})_2$ or $Si(R^{13})_3$, where

R^{13} are identical or different and are each C_1-C_{10} -alkyl, C_6-C_{15} -aryl, C_3-C_{10} -cycloalkyl, alkylaryl, where the radicals mentioned may be partially or fully substituted by heteroatoms,

R^8, R^{12}, R^8, R^{12} are identical or different and are each C_1-C_{10} -alkyl,

Y are oxygen $-O-$

R^7 is a $\{-Z(R^{15})(R^{16})\}_m$ - group, where

Z can be identical or different and are each silicon, germanium, tin or carbon,

R^{15}, R^{16} are each hydrogen, C_1 - C_{10} -alkyl, C_3 - C_{10} -cycloalkyl or C_6 - C_{15} -aryl,
and
 m is 1, 2, 3 or 4.

4. A process or complex as claimed in any of the preceding claims,
wherein the substituents R^8, R^9 and R^{12}, R^{12} are identical and are selected from among
methyl, ethyl, n-propyl, i-propyl, n-butyl, sec-butyl and tert-butyl, particularly preferably
methyl.

5. A process or complex as claimed in any of the preceding claims,
wherein the substituents R^1 and R^1 are identical or different and are each hydrogen or
methyl.

6. A process or complex as claimed in any of the preceding claims,
wherein M is zirconium.

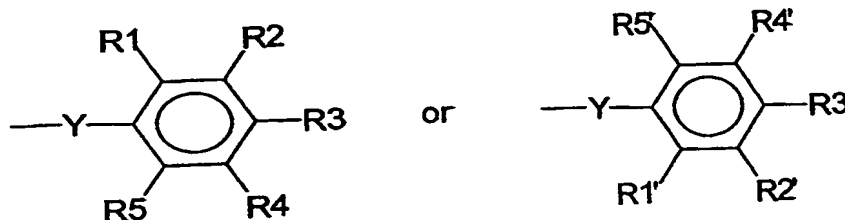
5 7. A process or complex as claimed in any of the preceding claims,
wherein M^2 is magnesium or lithium.

8. A process or complex as claimed in any of the preceding claims,
wherein R^7 is a dimethylsilyl group or an ethanediyl group.

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9. A process as claimed in any of claims 1, 2 and 4 to 8,
wherein, in a further step, the compound of the formula (I) is reacted with suitable re-
placement reagents to replace at least one of the groups

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by halogen substituents such as F, Cl, Br or I or by linear, branched or cyclic C_{1-10} -alkyl substituents.

25 10. A process as claimed in claim 9,
wherein the replacement reagents are selected from among aliphatic and aromatic car-
boxylic acid halides such as acetyl chloride, phenylacetyl chloride, 2-thiophenacetyl chlori-
de, trichloroacetyl chloride, trimethylacetyl chloride, O-acetylmandelyl chloride, 1,3,5-ben-
zenetricarboxylic chloride, 2,6-pyridinecarboxylic chloride, tert-butylacetyl chloride, chlo-
roacetyl chloride, 4-chlorobenzacetyl chloride, dichloroacetyl chloride, 3-methoxyphenyla-
cetyl chloride, acetyl bromide, bromoacetyl bromide, acetyl fluoride, benzoyl fluoride,
30 $SOCl_2$, silicon tetrachloride, organoaluminum compounds such as tri- C_1-C_{10} -
alkylaluminums, in particular trimethylaluminum, triethylaluminum, tri-n-butylaluminum, tri-
isobutylaluminum, and dialkylaluminum chlorides, aluminum sesquichlorides, methylalumi-
num dichloride, dimethylaluminum chloride, aluminum trichloride and ethylaluminum dichlo-
ride and combinations thereof.

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11. A process as claimed in claim 9,
wherein replacement reagents used are HF, HBr, HI, preferably HCl, as such or as solutions in water or organic solvents such as diethyl ether, DME or THF.

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12. A process as claimed in any of claims 1, 2 and 4 to 11,
wherein the deprotonating agent is selected from among n-butyllithium, tert-butyllithium, sodium hydride, potassium tert-butoxide, Grignard reagents of magnesium, magnesium compounds such as, in particular, di-n-butylmagnesium, (n,s)-dibutylmagnesium and other suitable alkaline earth metal alkyl and alkali metal alkyl compounds.

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13. A process as claimed in any of claims 1, 2 and 4 to 12,
wherein no intermediates are isolated during the process.

15. 14. A complex as claimed in claim 3 selected from among dimethylsilylbis(1-indenyl)zirconium bis(2,4,6-trimethylphenoxide), dimethylsilylbis(2-methyl-1-indenyl)zirconium bis(2,4,6-trimethylphenoxide), dimethylsilylbis(2-methyl-1-indenyl)zirconium bis(2,6-dimethylphenoxide), dimethylsilylbis(2-methyl-1-indenyl)zirconium bis(2,6-dimethyl-4-bromophenoxide) and ethanediylbis(1-indenyl)zirconium bis(2,4,6-trimethylphenoxide).

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15. The use of a racemic metallocene complex as claimed in any of claims 3 to 8 and 14 as a catalyst or as a constituent of a catalyst for the polymerization of olefinically unsaturated compounds or as a reagent or catalyst in stereoselective synthesis.

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